Large Diamonds Grown at High Pressure Conditions

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A technique has been established to grow large diamonds up to 2 cm. The crystals are bulky polyhedron with yellow, blue, green or brown color as well as colorless, which depend on impurities. The impurities incorporated into the diamond are limited, i.e. nitrogen, boron, nickel, cobalt, silicon and phosphorus.

I Introduction

Since announcement of success in diamond synthesis in 1955 [1], the technique has been improved dramatically, and a large amount of synthetic diamond is produced for commercial use in three forms, i.e. large single crystal, powder and polycrystalline compact. This article is, however, concerned with only large single crystals made by a growth technique named the temperature gradient method [2-4]. The largest diamond made so far is 34.8 carats (ca. 7g) [5], and 10 mm diamond is commercially available [6]. Synthetic diamond crystals have appeared in gem market [7], although they have not become popular.

This article summarizes the growth technique, and characteristics of the grown crystals are reviewed. Several review articles published already may also be helpful to learn more details of the diamond [8-16].

II Growth of diamond: the temperature gradient method

The temperature gradient method for growth of large synthetic diamonds was developed by the GE research group. A number of the diamonds are being made in many companies and research laboratories in these days, although details of the method are not opened from companies. Fig. 1 shows a cell assembly used in our laboratory. Carbon source, a seed crystal and a growth media made of metal solvent-catalyst are essential parts for the growth. They are placed in a carbon heater so that the carbon source sits at a higher temperature region than the seed. In a simple cylindrical tube heater shown in Fig. 1, temperature becomes highest at the center when electric current passes the heater, and, therefore, the carbon source is placed at the center.

NaCl powder compact prepared to fit with the other parts is filled in the graphite heater, surrounding the three components, i.e. carbon source, solvent-catalyst and seed crystal. Other materials may be available instead of NaCl if it is chemically inert to carbon and the metal. The seed crystal is embedded in the compact so that it contacts with the bottom of the metal.
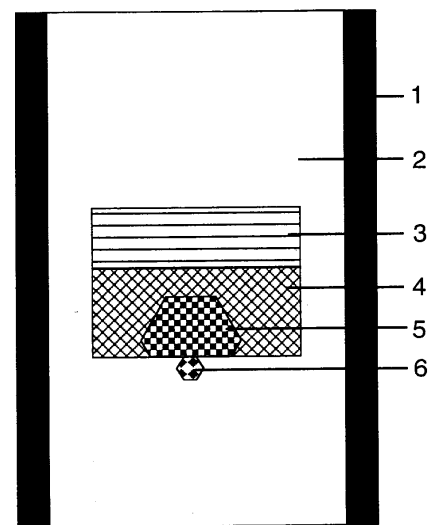

Figure 1. Sample assembly for diamond growth by the temperature gradient method. 1: Graphite heater, 2: NaCl pressure medium, 3: Carbon source, 4: Metallic catalyst-solvent, 5: Grown diamond, 6: Seed crystal.

The cell assembly is compressed up to 5 GPa in a high pressure vessel and then heated to 1500 °C. The pressure and temperature must be so high that the metal melts and that diamond is more stable than graphite. Precise control of pressure is not required, if pressure is high enough to grow diamond. If not, graphite grows instead of diamond. Some extents of

temperature control may be necessary, because it influences growth rates, incorporation of inclusion and impurities as described in following sections.

At the P, T condition, more than 10 atomic percent of carbon is dissolved into the molten metal up to saturation. In the presence of temperature gradient in the metal, solubility of carbon at the top of the molten metal which contacts with the carbon source is higher than that at the bottom of the metal, because the solubility increases with an increase of temperature. The solubility difference between the top and bottom of the metal causes dissolution of the carbon source and transportation of carbon from the carbon source to the seed crystal which contacts to the bottom of the metal, resulting in growth of new crystal on the seed. The temperature gradient is driving force to grow a crystal, and the crystal continues growing at a constant pressure and temperature.

Graphite disk or powder is used as the carbon source. The graphite converts to diamond in a few minutes after reaching the given temperature under the high pressure, and, therefore, diamond powder is also useful as the carbon source. Quality of graphite is not sensitive for the growth of diamond. However, low purity carbon is not available. It has been reported that hydrogen present in carbon has a poisonous effect [17]. According to the author's experience, a carbon material for a pencil did not convert to diamond. Additives such as resin or clay added to the carbon may deteriorate the ability of the metal solvent-catalyst for the conversion.

Carbon contains 1.1% of ^{13}C isotope with natural abundance. Isotopically pure or ^{13}C enriched carbon has been used as the carbon source to grow isotope modified diamonds. Thermal conductivity of the isotopically pure ^{12}C diamond has been found to be 50% higher than that of normal diamond with natural abundance isotope [18]. ^{13}C enriched diamond has helped to identify defect structures by optical spectroscopy and ESR [19,20]. When mixed isotopes are used, some absorption or luminescence peaks split or shift, suggesting the structure models.

A small single crystal of diamond is used as the seed. Size and quality influence growth rate and quality of the grown crystal as described in following sections [6,21].

Any material may be useful for the growth medium in which diamond grows. However, metals containing nickel, cobalt or iron as a main component are usually used [22]. They are called catalyst-solvent or catalyst. High reactivity with carbon and low melting temperature are main factors to be considered for selection of the growth medium. Copper has lower melting temperature than nickel, but the former has very low reactivity, and diamond is not grown with high growth rate [23,24]. Alloying is a way to decrease the melting temperature[3]. The melting temperature means the temperature at which liquid phase appears in the metal-carbon system. If the system is in eutectic relation, the liquid phase appears at a temperature lower than that of pure metal. On the other hand, if solid carbide is formed in the system, higher temperature is required to form liquid phase. Magnesium has also been used as the catalyst-solvent, but very high temperature, 1800^oC, is required, because magnesium carbide melts at such a high temperature [25].

III   Crystal size

Crystal size is roughly proportional to growing time, and, therefore, long time is required to grow a large crystal. Growth rate is influenced by temperature and temperature gradient. The growth rate increases with increasing temperature and/or temperature gradient. Higher growth rates may be desirable from a view point of production, but inclusions are readily incorporated at higher rates. Vagarali *et al.*[11] have summarized optimum growth rates at which good quality diamonds grow. A figure quoted by them shows good quality crystals up to 0.5 mg are made with growth rates of 1 to 3 mg/hr. De Beers and Sumitomo have made larger diamonds at higher growth rates; 14.2 carats for 500 hrs [11] and 10 carats for 150 hrs [6], respectively. This high growth rate was achieved with employing a large seed crystal of 5 mm in diameter. The world largest crystal is 34.80 carats made by De Beers in 1992.

Transportation of carbon in the growth medium has been simulated to calculate growth rates [26]. The study revealed that the growth rate has a maximum at an initial stage followed by a gradual decrease to a constant. Metallic inclusion is readily incorporated at the initial stage of growth because of the high growth rate. Li *et al.* [27] have proposed a modified cell assembly to suppress the incorporation of the inclusion. In the assembly, the metal solvent-catalyst has a lower part where diameter is small, resulting in lowering carbon supply.

IV   Morphology

Fig. 2 shows an example of a crystal grown on a seed. It has smooth surfaces except a bottom surface, which is rough because this surface had faced with inner wall of the NaCl growth cell. The smooth surfaces are indexed as {111} and {100}. In addition, {113} and {110} surfaces appear commonly as minor surfaces [3]. {115} and {117} have also been observed [3,28]. The morphology depends on growth temperature and composition of the metallic solvent-catalyst. {111} and {100} are known to appear most dominantly on synthetic diamond. When the surfaces are compared, {100} develop more dominantly than {111} at lower growth temperatures, whereas {111} is larger than {100} at higher temperatures [29]. A report says that {115} surfaces

appear when boron is doped [28]. According to author's experiments, they were seen on crystals grown from Co-Ti alloy at low temperatures.
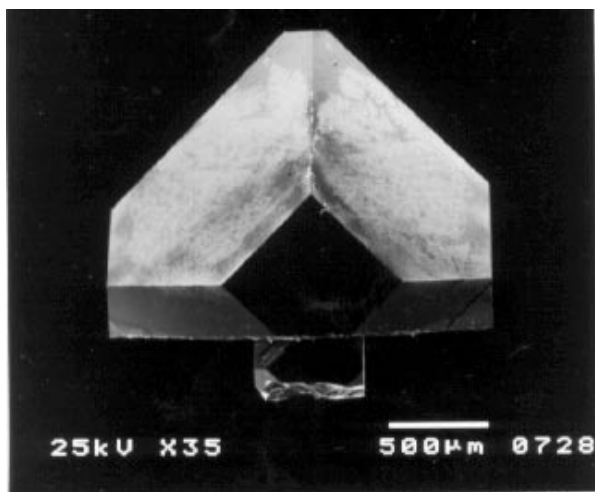

Figure 2. Diamond grown on a seed crystal. A small crystal at the bottom is the seed crystal with 0.5 mm in diameter. (Scanning electron micrograph).

Cross section of a grown crystal reveals growth history of the crystal because of inhomogeneous distribution of impurities [30]. An example is shown in Fig. 3. Change of area of each growth surface during growth can be determined from such a picture. A region, which is formed with piling up of a growth layer, seen on the cross section is named a growth sector. It has been demonstrated that fluctuation of growth condition influences morphology very sensitively [31].
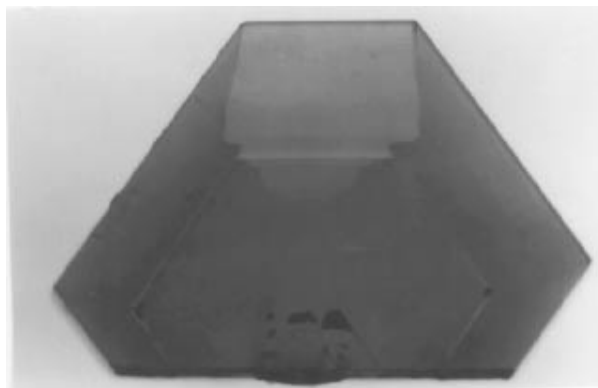

Figure 3. Cross section of a grown crystal after polished along (110) plane, taken under transmitted light. A (001) growth sector is paler yellow than adjacent {111} growth sectors which appear darker in this black and white picture. This picture shows that relative dimension of the (001) surface to {111} surfaces changed abruptly in a mid way of the growth.

Twin planes parallel to {111} are sometimes seen. If the seed crystal contains a twin plane, this extends to the grown crystal. Crystals containing numerous twin

planes have grown at lower temperatures according to our experiments, which looks to be an aggregates [32].

V   Growth surface

The growth surfaces appear smooth macroscopically, but fine patterns are revealed with aid of optical microscopes. Dendritic patterns are commonly seen on the synthetic diamonds commercially available [33]. The patterns depend on composition of the metallic solvent-catalysts, because they are reflected by textures formed when molten metals solidify [34]. A crystal grown from Fe-30%Ni alloy exhibits dendritic patterns with high symmetry. On the other hand, striations independent of orientation of diamond are seen on a crystal grown from iron. A growth hillock which suggests the spiral growth mechanism has been observed on a crystal, although it is not clearly seen because of the presence of the dendritic pattern [35]. However, cathodoluminescence topography showed a clear zoning which corresponds to vicinal surfaces of the growth hillock. The pattern suggests that the hillock consists of two types of vicinal surfaces, which have different luminescence nature caused by orientation dependent incorporation of impurities [36].

VI   Defects

Recently the growth technique has been sophisticated to produce defect free crystals [21], but a variety of defects have been observed depending on growth conditions. The defects are classified into four types; inclusion, stacking fault, dislocation and atomic impurities, which correspond to three-, two-, one- and zero-dimensional defects, respectively. The defects except for stacking fault are described in the following sections.

VI.1 Inclusion

Size of inclusions varies from 1 μm to 1 mm. The large inclusion is the metallic solvent-catalyst encapsulated by growing diamond, and have platy or rod like shape with round corner [37]. In order to suppress formation of the inclusion, lower growth rates are required. In general, inclusion is more readily captured at conditions where colorless crystals grow [2], and production cost of colorless crystal is higher than that of yellow crystals.

Micron size inclusions are also commonly present even in crystals which do not exhibit any metallic inclusions [37]. Dark field illumination is a sensitive method to detect the fine inclusions dispersing with low density. They are sometimes present as an aggregate. Chemical composition of the inclusions has not been identified definitely. Cobalt has been detected in an aggregate of the fine inclusions present in a crystal grown

from cobalt metal employing a micro-beam X-ray fluorescence technique [38]. However, the aggregate has a completely different form from the large inclusion, suggesting that the aggregate is of solid particles such as oxide or halides. It may be probable that they were trapped as solid particles which had dispersed in the molten metal. When titanium is added to the metallic solvent-catalyst as a nitrogen getter, TiC fine crystals are captured into grown crystal. Incorporation of the TiC crystal has successfully been suppressed by adding copper to the solvent-catalyst [39].

VI.2 Dislocation

A number of dislocations are observed even in inclusion free crystals [30]. Most of them extend to growth directions originating from the seed crystal. X-ray and cathodoluminescence topography techniques detect the dislocations clearly [40]. Local strain caused by dislocations is readily observed using a polarized microscope [41]. Recently crystals with low density dislocations have been made employing a dislocation free crystal as the seed crystal [21].

VI.3 Impurities in relation to color

Diamond captures limited kinds of elements as atomic impurities that become optical active centers. They are hydrogen, boron, nitrogen, silicon, phosphorus, nickel and cobalt. The impurities except hydrogen produce absorption and luminescence bands caused by electronic transitions. Optical properties associated with the impurities are described in the following sections. Hydrogen is the most major impurity for CVD diamond, but not for high pressure synthetic diamond, and this is omitted here.

VI.3.1 Nitrogen

Most of synthetic diamond commercially available exhibits yellow color. The yellow color is attributed to 50 to 500 ppm of nitrogen impurity [3,42], which are incorporated without intention, probably from high pressure media surrounding the growth cell. The nitrogen is incorporated as an isolated atom on diamond lattice site, producing strong absorption with a peak in a UV region, a tail of which extend to a visible region giving rise to yellow color. If a crystal is grown above 1500 ^{o}C, nitrogen impurities partly aggregate to pairs during growth [43]. More details on the aggregation are described below in this section. It may be possible to dope higher concentrations of nitrogen by adding nitrogen containing compounds. ^{15}N-enriched aniline has been added to a growth cell in order to study isotope shift of nitrogen related optical centers [44]. However, it is not easy to dope higher concentrations of nitrogen. 800 ppm of the nitrogen concentration is the highest in crystals grown from conventional metallic solvent-catalysts [45], in contrast that it is not rare for natural

diamond that more than 1000 ppm of nitrogen is contained. Recently more than 1000 ppm of nitrogen have been incorporated using non metallic catalyst, Na_2SO_4 [46]. Non-metallic catalysts are essential to dope high concentrations of nitrogen, because it is sure that natural diamond also grows from molten rocks, i.e. a kind of non-metallic materials. On the other hand, it is easy to reduce the concentrations of nitrogen to grow colorless crystals, using the metallic solvent catalysts.

In order to reduce the nitrogen concentrations, composition of the alloy used as solvent- catalyst is modified [3]. Ni, Co, Fe and their alloy produce diamond containing 50 to 300 ppm of nitrogen. With adding elements such as Ti, Zr and Al to the metals, concentrations of nitrogen are reduced. The elements are, therefore, called "nitrogen getter". A few percents of Ti additive is sufficient to grow a colorless crystal, in which nitrogen concentrations are less than 1 ppm. V, Cr and Mn, which sit at right positions of Ti in the priodic table, have also effect to reduce the nitrogen concentrations, but their power is lower than Ti [47]. Higher contents of the elements must be present in the metallic solvent-catalysts in order to grow colorless crystals.

The nitrogen concentrations in diamond may be related to chemical affinity of nitrogen with the solvent-catalyst metal. If the solvent-catalyst have strong affinity with nitrogen, more nitrogen stay in the solvent catalyst and less amounts of nitrogen are incorporated into diamond [47]. Another interpretation about the nitrogen getter effect has been proposed [39]; if the nitrogen getter elements are present in the solvent catalysts, nitrides such as TiN and ZrN are formed, and nitrogen concentrations in the molten metal becomes low, resulting in low concentrations in the growing diamond.

Growth temperature also influences nitrogen concentrations [29,48]. The nitrogen concentrations decrease with increasing growth temperature, when Ni or Co is used as the solvent-catalyst. On the other hand, the nitrogen concentrations increase with increasing growth temperature, when solvent-catalysts containing the nitrogen getters are used. This may be because the getter effect becomes weak at higher temperatures.

The influence of the catalyst-solvent and temperature in incorporation of nitrogen into diamond has been interpreted in terms of solubility of nitrogen in the catalyst-solvent metals [49]. If the solubility is large, more nitrogen stays in the metal and less nitrogen is incorporated into diamond. The solubility of nitrogen may be another word of affinity described above. The solubility increases with increasing temperature, resulting in a decrease of nitrogen concentrations.

Microscopic observation of the grown crystal gives us a finding of inhomogeneous distribution of the nitrogen related yellow color. Fig.3 is a cross section of a synthetic diamond, which exhibits regions with different depth of yellow color. Usually {111} growth sectors ex-

hibit the deepest yellow color [3]. Order of the depth of yellow color is; {111} > {100} > {113} = {110}. Precise comparison shows that {113} sectors contains more nitrogen than {110} [50]. There is a report that a crystal grown at low growth temperatures contains more nitrogen in {100} than in {111}[29], indicating that the nitrogen concentrations are influenced by temperature more sensitively in {100} sectors than in {111}. It may be interesting that nitrogen isotope ratio, $^{15}N/^{14}N$, in {111} sectors is different from that in {100}[51].

The nitrogen related yellow color fades with heat treatment above 1500 ^{o}C, because single substitutional nitrogen atoms migrate to be pairs in the crystal [52]. With heating above 2500 ^{o}C, the nitrogen pairs convert to another aggregates, which are proposed to consist of four nitrogens and a vacancy [53]. The heat treatment must be carried out under high pressure conditions, 5 to 8 GPa, in order to prevent from graphitization. Most of colorless natural diamonds contain significant amounts of nitrogen in the aggregated forms, whereas colorless synthetic diamonds are nitrogen free. It is well established that natural diamonds have been heat-treated in the Earth so long that the nitrogens have been aggregated. Measurements of the aggregation rate of nitrogen help us to estimate age of natural diamond [13,54].

The aggregation rate determined for the first time was based on the second order kinetics [52]. The report on the kinetics gave ppm^{-1} value of kinetic coefficient of $1.74 \times 10^{-4}(min^1/ppm^{-1})$ at 1900°C, which corresponds to 50% of conversion of single forms to pairs of 100 ppm nitrogen with heat treatment at 1900 ^{o}C for lhr.

The aggregation rate is a function of temperature, but it has become apparent the temperature is not only a factor which influences the aggregation rate. The aggregation rate strongly depends on growth sectors. There is a report showing that it is higher in {111} sectors than in {100} [29]. It has also been presented that the aggregation rate is not uniform even in a growth sector [55]. The non uniformity are suggested to be attributed to inhomogeneous distribution of other defects [56]. It has been pointed out that the second order kinetics can not be applied for the aggregation process [57,58]. Further study is required to understand the aggregation process.

Nitrogen impurities produce absorption and luminescence peaks other than that giving the yellow color [9,16], common ones of which are the N3 center (zero-phonon peak at 415 nm) consisting of three nitrogens and a vacancy, the H3 center (zero-phonon peak at 503 nm) consisting of two nitrogens and a vacancy, 575 nm zero-phonon peak caused by a nitrogen and vacancy, and the NV center with a zero-phonon peak at 637 nm. These are produced by irradiation of high energy beam such as electron and neutron followed by heat treatment. However, it is not unusual that these are observed in unirradiated crystals. Lattice distortion may

produce these bands [59]. It is well known that the H3 luminescence band is present in {100} sectors of as-grown synthetic diamond commercially available [30].

VI.3.2 Boron

Incorporation of boron impurity produces blue color in diamond [50, 60-62] and the diamond has p-type semiconducting property. The color is given by a gradual increase of absorption from high energy to low energy in a visible region. No sharp peak is present in the visible region, but sharp absorption peaks are seen around 3.5 μm of an infrared region [63].

The blue color diamond is readily made, if a small amount of boron is added in a growth cell [50]. Depth of blue color increases with increasing the boron additives. However, more amounts of boron additive are required to produce blue color, when diamond is grown from metal solvent catalysts without nitrogen getter, because boron acceptor is compensated by nitrogen donor and only uncompensated acceptor contributes to blue color.

According to our experience, when pure nickel which produces diamond containing 200 to 300 ppm of nitrogen was used, more than 10 mg of boron was required to be added into the growth cell in order to grow blue colored diamond. Yellow color persisted when less than 10mg boron was added. On the other hand, addition of 0.1 mg of boron was enough for growth of the blue colored crystal when the solvent catalyst was Ni-3%Ti, from which nitrogen free crystal was grown.

The blue color is not uniform even in a crystal. Growth sector dependence is observed. {110} sectors most sensitively change to blue, when boron is added, whereas {111} sectors are the most insensitive. The {111} sectors persist yellow color, if boron additive is not sufficient. However, {111} sectors become the deepest in sectors, when a large amount of boron is added. Namely, the order of depth of blue changes with an increase of boron additive. The sector dependence is understandable, if we assume two factors; (1) {111} sectors capture both boron and nitrogen most easily and (2) depth of blue color is proportional to uncompensated boron, i.e. [boron]-[nitrogen], where the brackets indicate the concentrations of boron and nitrogen. As for {111} sectors, if boron additive is little, the concentration is lower than that of nitrogen, resulting in persistence of yellow color. If boron additive is large, the concentrations of uncompensated boron become the highest.

The boron doped diamonds give bluish green luminescence with electron beam excitation (cathodoluminescence), in which four broad bands are present in UV and visible regions [64]. Bound exciton peaks are also observed in a UV region of 230 to 240 nm. UV illumination produces broad phosphorescence bands peaking at 2.1 and 2.5 eV from the boron doped crystals. They decay slowly [65]. About 1 minute of life time has been recorded.

VI.3.3 Nickel

More than ten of optical bands have been documented from diamond grown from nickel containing alloys. The nickel related bands are also dependent on concentrations and structure of nitrogen impurities. A diamond grown from pure Ni exhibits brownish yellow color, and zero-phonon peaks at 2.51 eV, 1.883 eV and 1.4 eV are seen in absorption spectra recorded at a liquid nitrogen temperature [66,67]. In contrast, diamond grown from iron does not produce any sharp peak in spite of having similar yellow color. A monotonic increase in absorption to a UV region is observed. When nitrogen getters such as Ti are added to nickel, green or brown crystals grow, in which characteristic absorption peaks, which are different from those observed from pure Ni, are observed [68,69].

The crystals containing nickel also give unique luminescence bands [67]. Zero-phonon lines of the bands are at 2.56 eV and 1.4 eV. The latter is observed in absorption spectra as well. This peak has been confirmed to be related to Ni from isotope splitting measured by high resolution spectroscopy [70].

ESR studies have determined concentrations and structure of nickel impurities in pre- annealed crystals [20, 71]. Ni^{-1} which substitutes a carbon atom on diamond lattice has been detected. The highest concentration measured so far is 70 ppm. Interstitial Ni^+ has also been detected. Correlation between the Ni impurities and the optical bands have not been well established, although it has recently been reported that the concentrations of Ni^{-1} is proportional to intensity of the 2.51 eV peak [72].

The nickel containing crystals change their color with heat treatment above 1500 ^{o}C. The brownish yellow color changes to brown, in which a number of sharp absorption peaks are observed [73]. The green color also becomes brown. This brown colored crystal does not have characteristic peaks, but strong green color luminescence is produced by UV illumination, and several luminescence peaks have been recorded [74-76]. The color change produced by the heat treatment is related to migration of nitrogen impurities to form complexes with nickel impurity [74]. Structure models of the complexes consisting of nickel, nitrogen and vacancy have been proposed, based on ESR measurements [74-77].

The nickel related optical centers are located only in {111} growth sectors [68,78]. X-ray fluorescence technique has also detected the nitrogen impurity in synthetic diamonds, and has confirmed that the nickel is confined to {111} growth sectors [79]. Detailed observation has revealed that it is not uniform even in a (111) sector. The colors become deeper in regions which grew at higher growth rates [48].

VI.3.4 Cobalt

The X-ray fluorescence technique has also detected cobalt impurity in diamond grown from cobalt [80]. It is located only in {111} growth sectors as nickel impurity is. However, unique absorption band is very weak, but strong yellow luminescence is observed from the crystals after heat treated [81]. Several luminescence peaks have been seen in photo- and cathodo-luminescence spectra. The peaks depend on degrees of aggregation of nitrogen. Cobalt impurities have been less studied compared with nickel.

VI.3.5 Silicon

Silicon impurity produces only one peak at 1.681 eV in both absorption and luminescence. It is observed in CVD diamonds commonly, because silica glass and silicon is usually used in a reaction cell and a substrate, respectively [82]. It has also been observed in Si ion implanted diamond [83]. As for high pressure diamond, the peak is produced, when silicon containing alloys are used as the metallic catalyst-solvents. The peak was sharper than those observed in the CVD diamond, which made a precise investigation possible [84]. The peak split to 12 lines corresponding to natural abundance silicon isotope by high resolution spectroscopy. This is a direct evidence that silicon impurity is involved in the 1.681 eV center. Structure model of the silicon related defect has not been established, although it has been proposed that a vacancy is also involved.

VI.3.6 Phosphorus

n-Type semiconducting diamond has been made with doping phosphorus by the plasma assisted chemical vapor deposition (CVD) technique [85]. The phosphorus impurity incorporated in the crystal has been detected by the SIMS technique, and a unique cathodo-luminescence peak at 5.175 eV in a UV region has been detected, which is expected to be of a bound exciton of phosphorus donor [86]. However, phosphorus elements or phosphorus related optical centers have not been found in the large crystals grown by the temperature gradient method. A complex of phosphorus and nitrogen has been detected by ESR in a crystal grown from pure phosphorus under a high pressure condition, although the grown crystal investigated is a very thin layer formed on a seed crystal [87].

VII   Conclusion

Since announcement of success in large diamonds by the temperature gradient method in 1970, the technique has been improved to produce 10 mm crystals and defect free crystals in a commercial scale. Some kinds of defect tuning have become possible. Then, the crystals are available for both industrial applications and scientific study. However, a problem we have is production cost. Diamond is still an expensive material compared with the other materials. Further improvement of the

growth technique and an increase of demands to the crystals will allow us to produce the diamonds with cheaper cost.

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